Nonbenzenoid Aromatic Systems. VIII.[1a] Buffered Acetolysis of 2-(4- and 2-(6-Azulyl)ethyl Arenesulfonates and 3-(4-Azulyl)-1-propyl Nosylate. Examples of Ar_3-5 and Ar_3-6 Mechanisms

Richard N. McDonald,* N. Lee Wolfe, and Herbert E. Petty[1b]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

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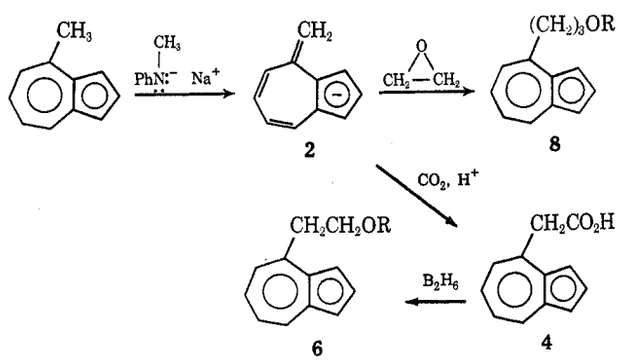
2-(4- (6) and 2-(6-Azulyl)ethyl (7) tosylates and nosylates were synthesized and subjected to buffered acetolyses. The k_{RONs}/k_{ROTs} ratio for these two systems was found to be 2.1–3.3 compared to 10–13.5 found for this ratio for 2-phenylethyl, 2-(*p*-anisyl)ethyl, and ethyl tosylates and nosylates. The reduced value for this ratio for the derivatives of 6 and 7 was caused by elimination to the corresponding vinylazulenes competing with solvolysis, $k_t = k_{solv} + k_{elim}$. Deuterium labeling in the 7-α,α-d_2-OTs after one solvolytic half-life showed no methylene scrambling in recovered 7-d_2-OTs or 7-d_2-OAc, whereas 7-α,α-d_2-ONs gave about 10% methylene scramble in both the nosylate and acetate. 6-α,α-d_2-ONs gave 0% label scramble under the same conditions. Azulene ring C_3 participation is argued for to explain this latter result for 6-ONs buffered acetolysis to form the tricyclic Ar_3-5 intermediate (15). To substantiate this proposal of producing 15, the buffered acetolysis of 2-(4-azulyl)propyl nosylate (8-ONs) was found to yield 4,5-dihydro-3*H*-benz[*cd*]azulene (18, 72%) and 8-OAc (27%). The kinetic data and activation parameters for these systems are discussed.

One of several interesting features in the use of the nonbenzenoid, nonalternate aromatic azulene nucleus in studying reactions potentially involving neighboring aromatic group participation is that the azulene ring has five structurally and chemically nonequivalent sites for attachment of the side chain containing the reaction center. We recently demonstrated that the 1-azulyl substituent in the buffered acetolysis of 2-(1-azulyl)ethyl OTs (1) is a *super power* in β-aryl participation in 2-arylethyl arenesulfonate solvolyses with exclusive reaction *via* the k_Δ pathway (the ionization step was rate determining) without the complicating factor of ion-pair return.[2,3]

The 1 and 3 positions of azulene are the sites of largest π-electron density[4] and have the smallest cation localization energy[4a] in the ground state. They are unique ring positions in that when bonded to an electrophile the intermediate is another "aromatic" system, the azulenium ion (a substituted vinyltropylium ion).[4a,5]

We now wish to report the results of buffered acetolyses of primary ω-azulylalkyl arenesulfonates with the alkyl side chain attached to the π-electron-poor azulene 4 and 6 positions.[4]

Substrate Syntheses.—The preparation of the ω-azulylalkanols took advantage of the relative acidities of the methyl group C–H bonds when attached to the azulene 4 and 6 positions.[6] Proton abstraction from 4- and 6-methylazulene with sodium *N*-methylanilide gave sodium 4- (2) and 6-methyleneazulenate (3),[6,7] respectively, which when carbonated produced 4- (4) and 6-azulylacetic acid (5), respectively.[6a] Reduction with diborane yielded the corresponding ethanols, 6-OH and 7-OH; deuteriodiborane reduction of 4 and 5 produced the α,α-dideuterioethanols, 6-OH-α,α-d_2 and 7-OH-α,α-d_2. 3-(4-Azulyl)-1-propanol (8-OH) was synthesized by allowing 2 to react with ethylene oxide.



The tosylate esters were prepared by the ether–powdered potassium hydroxide method.[8] The nosylate esters were prepared by allowing the alcohol to react with methyllithium in ether, producing the alkoxide, which was treated with *p*-nitrobenzenesulfonyl chloride.

Discussion of Kinetic and Product Results from 6 and 7 Arenesulfonates.—Potassium acetate buffered acetic acid (20% excess buffer) was the solvolytic medium used in these studies. The presence of the buffer is sessential owing to the basicity of azulene to strong acid producing azulenium ions. Potassium acetate has been shown to exert a special salt effect in the acetolysis of 2-(*p*-anisyl)ethyl OTs which may also be present in the buffered acetolysis of 1.[2] The kinetic buffered acetolysis data for arenesulfonates of 6-OH and 7-OH and their activation parameters are listed in Table I.

The initial studies involved the tosylates 6-OTs and 7-OTs to allow a direct comparison with 1. The rate constants for 6-OTs and 7-OTs were very similar and about 10^4 smaller than that of 1 at 110°. On the other hand, they were of the same order of magnitude

(1) (a) For paper VII see R. N. McDonald and H. E. Petty, *J. Org. Chem.*, **37**, 2957 (1972). (b) Phillips Petroleum Co. Fellowship, 1968–1969.

(2) R. N. McDonald and J. R. Curtis, *J. Amer. Chem. Soc.*, **93**, 2530 (1971).

(3) For a review on phenonium ions see C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer in "Carbonium Ions," Vol. 3, P. v. R. Schleyer and G. A. Olah, Ed., Interscience, New York, N. Y., 1972.

(4) For example see results of MO calculations in (a) E. Heilbronner in "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience, New York, N. Y., 1959; (b) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 456–457.

(5) 1-Azuloic acid has been shown to be a considerably weaker acid than benzoic acid, $\Delta pK_a = 1.2$: R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **37**, 2703 (1972).

(6) (a) K. Hafner, H. Pelster, and H. Patzett, *Justus Liebigs Ann. Chem.*, **650**, 80 (1961); (b) M. Scholz, L. Vien, G. Fischer, B. Tschapke, and M. Muhlstadt, *Chem. Ber.*, **100**, 375 (1967).

(7) The term azulenate refers to the general structure of the anion in the salts produced by such α-proton abstractions from 4- and 6-alkylazulenes[6a] and by nucleophilic additions to the azulene ring 4 and 6 positions.

(8) K. B. Wiberg and A. J. Ashe, *J. Amer. Chem. Soc.*, **90**, 63 (1968).

TABLE I

BUFFERED ACETOLYSIS KINETIC DATA FOR 2-(4- AND 2-(6-AZULYL)ETHYL TOSYLATES AND NOSYLATES

Compd	Temp, °C	10^5k,[a] sec^{-1}	Av 10^5k, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu	k_{RONs}/k_{ROTs} (120°)
6-OTs[b]	140.0	22.5 ± 0.3	22.2			
		22.0 ± 0.5				
	120.0	5.60 ± 0.3	5.61	21.4 ± 0.5	−24.7 ± 1.0	
		5.62 ± 0.12				
6-ONs[b]	130.0	25.7 ± 0.8	26.0			
		26.3 ± 0.2				
	110.0	5.20 ± 0.01	5.18	24.0 ± 0.4	−16.1 ± 0.6	
		5.17 ± 0.06				
	120.0		(11.8)[c]			2.1
7-OTs[b]	140.0	25.4 ± 1.0	24.9			
		24.3 ± 0.5				
	120.0	5.67 ± 0.2	5.63	23.2 ± 0.5	−19.6 ± 1.3	
		5.58 ± 0.08				
7-ONs[b]	130.0	40.2 ± 0.2	40.0			
		39.8 ± 2.0				
	110.0	8.2 ± 0.4	8.3	23.4 ± 0.1	−16.5 ± 0.3	
		8.3 ± 0.4				
	120.0		(18.6)[c]			3.3

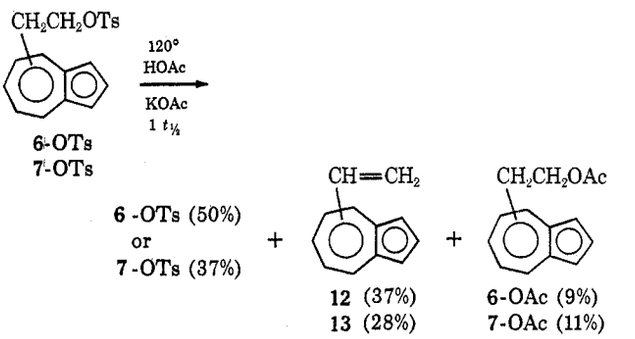
[a] Rate constants with standard deviations based on experimental infinity titers; using theoretical infinity titers, rate constants for derivatives of **6** and **7** increase by ~10%. [b] Sealed ampoule method, potentiometric titrations; 0.005 *M* ROX, 0.006 *M* KOAc. [c] Extrapolated.

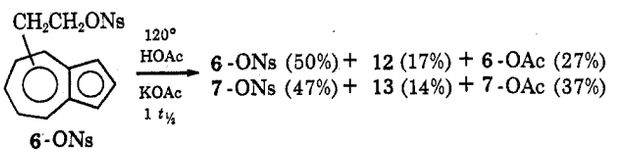
as the rate constant for unbuffered acetolysis of 2-phenylethyl OTs at 115° ($k_t = 1.27 \times 10^{-5}\ sec^{-1}$).[9]

The relatively high temperatures required for reasonable rate measurements for **6**-OTs and **7**-OTs presented a special problem with these substrates and their products. After about one solvolytic half-life, ampoules of samples of each tosylate began to change color and after several half-lives a green (from **6**-OTs) or brown (from **7**-OTs) insoluble material formed a coating on the ampoule wall. Since *p*-nitrobenzenesulfonate (nosylate = Ns) esters contain a better leaving group, $^-$ONs, than tosylate esters, it was decided to change to the nosylate derivatives with the hope of significant temperature reduction required for their buffered acetolyses.

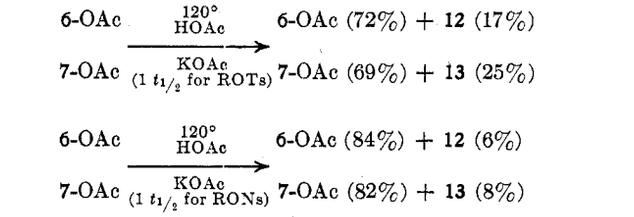
To acquaint ourselves with the preparation, handling, and solvolytic behavior of nosylate esters, we synthesized and subjected to buffered acetolyses 2-phenylethyl (**9**-ONs), 2-(*p*-anisyl)ethyl (**10**-ONs), and ethyl nosylate (**11**-ONs) along with the corresponding tosylate esters. The rate data and activation parameters for these three systems are listed in Table II. One point of immediate interest from the data in Table II is the reasonably constant value of k_{RONs}/k_{ROTs} = 10–13.5 for both nonparticipating and aryl participating buffered acetolyses. (The ratio for **10** may be somewhat high owing to the increased special salt effect in **10**-ONs with increased concentrations.) These ratios are in marked contrast to the k_{RONs}/k_{ROTs} = 2–3 found for the arenesulfonates of **6** and **7**.

To understand the reason for this reduced nosylate/tosylate rate ratio, we must examine the products derived from **6** and **7**. After one solvolytic half-life, the major products from **6**-OTs and **7**-OTs were 4-vinylazulene (**12**) and 6-vinylazulene (**13**), respectively, the product of elimination. The low recovery of **7**-OTs has been duplicated and is not understood, since the infinity titer is ~91% of theoretical and no deviation from linearity of the rate *vs.* time is observed. The nosylates, **6**-ONs and **7**-ONs, also underwent elimination to **12** and **13**, respectively, but to a smaller extent. A complicating feature of this reaction is that the acetates, **6**-OAc and **7**-OAc, also undergo elimination





to **12** and **13**, respectively, under the buffered acetolysis conditions.



We can see from the results of these product studies that elimination to the vinylazulenes **12** and **13** is the major reaction pathway from the tosylate esters. With the nosylate esters, solvolysis to the corresponding acetates becomes competitive with elimination. The probable reason why elimination is so prevalent

(9) J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *J. Amer. Chem. Soc.*, **91**, 1154 (1969).

TABLE II

BUFFERED ACETOLYSIS DATA FOR 2-PHENYLETHYL, 2-(*p*-ANISYL)ETHYL, AND ETHYL TOSYLATES AND NOSYLATES

Compd	Temp, °C	10^5k,[a] sec^{-1}	Avg 10^5k, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu	k_{RONs}/k_{ROTs}
9-OTs[c]	130.0	4.93 ± 0.21	5.03			
		5.13 ± 0.08				
	110.0	0.980 ± 0.008	0.988	24.2 ± 0.2	−18.8 ± 0.4	
		0.995 ± 0.004				
9-ONs[c]	110.0	11.4 ± 0.1	11.3			11.4
		11.1 ± 0.1				
	90.0	1.85 ± 0.02	1.85	24.3 ± 0.2	−13.6 ± 0.4	
		1.85 ± 0.01				
10-OTs[b]	95.0	13.6 ± 0.3	14.1			
		14.6 ± 0.6				
	75.0	1.99 ± 0.04	2.01	24.1 ± 0.5	−11.2 ± 1.3	
		2.03 ± 0.05				
10-ONs[c]	75.0	27.0 ± 0.3	27.1			13.5
		27.1 ± 0.2				
	55.0	3.17 ± 0.04	3.18	23.6 ± 0.1	−7.3 ± 0.2	
		3.18 ± 0.02				
11-OTs[b]	140.0	22.1 ± 0.5	21.9			
		21.6 ± 0.4				
	120.0	4.82 ± 0.04	4.78	23.7 ± 0.3	−18.5 ± 0.7	
		4.73 ± 0.05				
11-ONs[b]	120.0	47.5 ± 0.2	46.8			9.8
		46.0 ± 0.3				
	100.0	9.59 ± 0.05	9.57	22.4 ± 0.3	−17.4 ± 0.8	
		9.55 ± 0.07				

[a] Rate constants with standard deviations based on experimental infinity titers. [b] Sealed ampoule technique, potentiometric titrations; 0.005 *M* ROX, 0.006 *M* KOAc. [c] As per *b* but 0.010 *M* ROX, 0.012 *M* KOAc.

with derivatives of **6** and **7** is the increased acidity of β-CH bonds of the ethyl side chains compared to other 2-arylethyl derivatives.[6]

While insufficient data are available to completely analyze the component process, k_{solv} and k_{elim}, in the buffered acetolyses of **6** and **7** arenesulfonates, it should be noted that the rate data from which the rate constants listed in Table I are derived show good linearity throughout the two half-lives followed from either plots of the data or examination of the calculated instantaneous first-order rate constants in the computer output. If we make three simplifying assumptions, (1) both k_{solv} and k_{elim} are first-order or pseudo-first-order reactions,[10] (2) **6**-OAc is stable to the reaction conditions except toward elimination to **12**, and (3) the amount of k_{solv} is represented by the quantity of **6**-OAc isolated after one half-life, we can estimate k_{solv} in these reactions. Since about 21% of the product from **6**-OTs is **6**-OAc formed by k_{solv}, this percentage of the k_t for **6**-OTs would be $\sim 1 \times 10^{-5}$ sec^{-1} at 120°, which is essentially the value expected for the solvent-assisted (k_s) process for **9**-OTs under these conditions.[11] This approach applied to k_t for **6**-ONs gives k_{solv} $\sim 7 \times 10^{-5}$ sec^{-1} at 120° and a k_{RONs}/k_{ROTs} of 7 for **6**, in reasonable agreement with those ratios listed in Table II. Similar analyses of the k_t's of the arenesulfonates of **7** lead to k_{solv} $\sim 1 \times 10^{-5}$ sec^{-1} (120°) for **7**-OTs and $\sim 1 \times 10^{-4}$ sec^{-1} (120°) for **7**-ONs; however, these estimates for **7** are further clouded by the low recovery of especially **7**-OTs for unknown reasons. Assuming that the above analysis is reasonable, it would appear that the major influence of the change in leaving group in going from **6**-OTs to **6**-ONs is felt in k_{solv} rather than k_{elim}.[12a]

In the activation parameters for tosylates and nosylates of **9**-OH, **10**-OH, and **11**-OH listed in Table II, while the $\Delta H^{\pm}$'s are reasonably constant, the $\Delta S^{\pm}$'s show what appears to be a trend toward more positive values for the two substrates which have been shown to involve at least partial β-aryl participation in their acetolyses.[9,11,12b] This same trend is seen with the derivatives of **7** and most particularly with the arenesulfonates of **6**, with the latter substrates showing an increase in $\Delta H^{\pm}$ also. However, since elimination to the vinylazulenes is a major pathway from the tosylates and remains important in the nosylates, it is impossible at present to ascertain the meaning of these changes in $\Delta H^{\pm}$ and $\Delta S^{\pm}$ in the azulene substrates.[12b]

To determine if the azulene 4 and 6 positions were participating by the Ar_1-3 (k_Δ) pathway in the acetolyses of the arenesulfonates of **6** and **7**, respectively, the corresponding α,α-dideuterium derivatives were prepared and acetolyzed in the buffered acetic acid. The data are listed in Table III. As predicted from the analysis of the magnitude of k_{solv}, **7**-OTs contains only a negligible amount of the Ar_1–3 pathway after one solvolytic half-life. However, **7**-α,α-d_2-ONs showed about 10% scramble, which is strikingly similar to labeling results obtained in buffered acetolysis of **9**-OTs,[9] indicating the probable presence of Ar_1-3 participation by the azulene ring 6 position.[13] Considering the similar

(10) It would appear that this is a gross oversimplification in the case of k_{elim}.

(11) J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **91**, 7508 (1969), list $k_s = 7.3 \times 10^{-6}$ sec^{-1} for **9**-OTs in unbuffered acetic acid at 115°, and have shown k_s to be reasonably independent of ring substituents.

(12) (a) A. K. Colter and R. D. Johnson, *ibid.*, **84**, 3289 (1962), reported k_{RONs}/k_{ROTs} = 20 for the second-order rate constants in the reaction of 2-pentyl arenesulfonates with sodium ethoxide in ethanol at 50°. (b) No attempt to build an argument for or against aryl participation based on such small absolute changes in these $\Delta S^{\pm}$'s is implied, since these calculated values are subject to several possible errors.

(13) The percentages of methylene scrambling in recovered **7**-d_2-ONs and product **7**-d_2-OAc show that ion-pair return from the ethylene-6-nzulenium nosylate ion pair is important with $F \approx 0.3$–0.4 (120°). For unbuffered acetolysis of **9**-OTs, F = 0.37 (115°) was reported.[9]

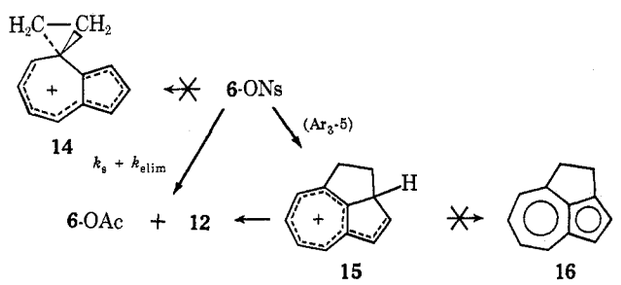
TABLE III
DEUTERIUM LABELING RESULTS FROM ARENESULFONATES AT 120° AFTER APPROXIMATELY ONE BUFFERED ACETOLYSIS HALF-LIFE[a]

Starting compd	% Scrambling[b,c] in ROAc	% Scrambling[b,c] in ROTs or RONs
7-α,α-d_2-OTs	1	>1
7-α,α-d_2-ONs	10	12
6-α,α-d_2-ONs	0	0

[a] Buffered acetic acid containing 20% molar excess KOAc. [b] Per cent scrambling determined by nmr integration of α- and β-methylenes *vs.* an internal standard and having a maximum of 50% ignoring any kinetic isotope effects. [c] Values considered to have error of ±1–2%.[13]

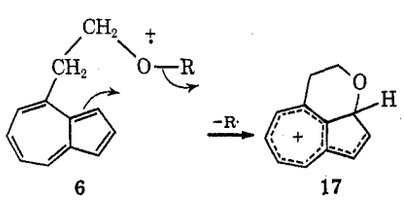
reactivities of the derivatives of **6** and **7**, we were surprised to find that 6-α,α-d_2-ONs showed no evidence of scrambling the α- and β-methylene groups by Ar_1-3 participation (**14**).

The total accumulated data, however, are consistent with at least partial ring participation for the buffered acetolysis of **6**-ONs. We suggest that this participation is of the Ar_3-5 type at the electron-rich ring C_3 position leading to tricyclic cation **15**. Reaction of **15** with the solvent must then occur at C_α of the former ethyl side chain to rearomatize with relief of strain to yield **6**-OAc rather than by proton abstraction to give **16**. It is also possible that proton abstraction



from C_β of the former ethyl side chain could occur to produce **12**. The potential presence of this latter pathway to **12** (presumably of the E1 type) would have the effect of increasing k_{solv} and reducing k_{elim} for **6**-ONs; a similar effect also cannot be ruled out for **6**-OTs.

The formation of tricyclic cation **15** had been proposed to explain the relative abundances of γ cleavage of $M\cdot^+ - TsO\cdot$, $M\cdot^+ - AcO\cdot$, and $M\cdot^+ - HO\cdot$ in the mass spectral fragmentations of **6**-OTs, **6**-OAc- and **6**-OH relative to the corresponding derivatives of **1**-OH and **7**-OH.[14] Of even greater significance was the $M\cdot^+ - Ts\cdot$, $M\cdot^+ - Ac\cdot$, and $Ac\cdot$, and, to a lesser extent, $M\cdot^+ - H\cdot$ fragmentations for the respective derivatives of **6**. These latter three fragmentation processes were characterized as being accompanied by bond formation with the ring C_3 position yielding tricyclic cation **17** and predicted ring C_3 participation



(14) R. G. Cooks, N. L. Wolfe, J. R. Curtis, H. E. Petty, and R. N. McDonald, *J. Org. Chem.*, **35**, 4048 (1970).

in the solvolysis of derivatives of 3-(4-azulyl)-1-propanol (**8**-OH).[14]

Buffered Acetolysis of 3-(4-Azulyl)-1-propyl Nosylate (8-ONs).—To substantiate the proposed intermediacy of **15** in the buffered acetolysis of **6**-ONs and the predictions from the mass spectral fragmentation data given above, we have examined the buffered acetolysis of **8**-ONs; the rate data are listed in Table IV.[15]

TABLE IV
BUFFERED ACETOLYSIS KINETIC DATA FOR 3-(4-AZULYL)-1-PROPYL NOSYLATE (8-ONs)

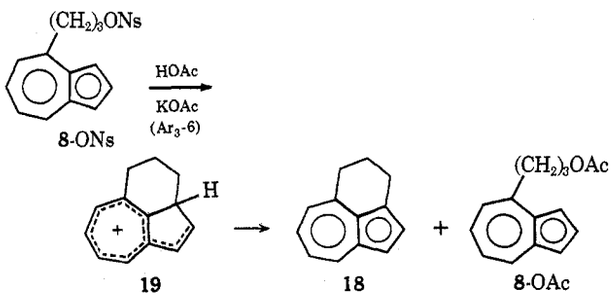
Temp, °C	10^5k,[a,b] sec^{-1}	Av 10^5k, sec^{-1}	$\Delta H^\pm$, kcal/mol	$\Delta S^\pm$, eu
120.0	127 ± 1	126		
	124 ± 6			
100.0	16.9 ± 0.7	17.1	28.5 ± 0.5	−1.0 ± 1.3
	17.3 ± 0.3			

[a] Rate constants with standard deviations based on experimental infinity points. [b] Conductometric method;[15] 0.0010 *M* ROX, 0.0012 *M* KOAc.

Compared to k_{solv} for **6**-ONs, **8**-ONs is characterized by an increase in rate by a factor of about 11 at 120°. The large, positive changes in both $\Delta H^\pm$ and $\Delta S^\pm$ for the buffered acetolysis of **8**-ONs compared to those for the tosylate and nosylate derivatives of **6**-OH, **7**-OH, **9**-OH, **10**-OH, and **11**-OH strongly indicate ring participation in the ionization of **8**-ONs.

The products from **8**-ONs isolated after 10 buffered acetolysis half-lives at 120° were 4,5-dihydro-3*H*-benz[*cd*]azulene (**18**) (51%), **8**-OAc (25%), and trace quantities of acylation products of **18** and **8**-OAc. Acetate **8**-OAc was shown *not* to arise from **18** under the acetolysis conditions; however, **18** was labile to the 10 $t_{1/2}$ acetolysis conditions at 120° with only 67% recovery. This corrects the yield of **18** produced from **8**-ONs to about 72%.[16] The isolation of **18** confirms participation by ring C_3 in the ionization of **8**-ONs.

Acetate **8**-OAc was also shown to be somewhat unstable to the acetolysis conditions at 120° with 91% recovery after 10 solvolytic half-lives. Using the previously mentioned approximations,[16] the amount of **8**-OAc produced from **8**-ONs was 27%. From the magnitude of $\Delta S^\pm$ (−1.0 ± 1.3), the formation of the entire amount of **8**-OAc by a k_s pathway seems unlikely. We suggest that both **18** and **8**-OAc are produced from **19** by proton abstraction and attack at C_1 of the former propyl side chain, respectively, by the solvent. This proposal is similar to the one sug-



(15) R. N. McDonald and G. E. Davis, *ibid.*, **38**, 138 (1973).

(16) The stability check of **18** is, of course, based on a full 10 solvolytic half-lives, while, from the acetolysis of **8**-ONs, a sizable concentration of **18** will only be present after ~1 solvolytic half-life. Assuming a linear rate of destruction of **18** with time and using 9 solvolytic half-lives as the basis for calculation, the amount of **18** produced in the buffered acetolysis of **8**-ONs was 72%.

gested for the destruction of intermediate **15** except that in the present case the tricyclic hydrocarbon **18** is more favorable in the product-forming reactions from the intermediate.[17]

Although a synthesis of **18** had been reported,[18] we felt that it was crucial to the present study to fully characterize the compound. The nmr spectrum of **18** [(CCl_4, internal TMS): τ 1.8–3.3 (azulyl H's, 6), 6.85 (t center, 4), and 7.87 (quintet center, 2)], while consistent with the tricyclic structure, was interesting in that both methylenes attached to the ring exhibited the same chemical shifts.[19] The visible λ_{max} for **18** and certain dimethylazulenes are listed in Table V and

TABLE V
VISIBLE λ_{max} OF CERTAIN ALKYL-SUBSTITUTED AZULENES

Compd	λ_{max}, nm
Azulene	580[a]
4,5-$(CH_3)_2$Az	578[a]
4,7-$(CH_3)_2$Az	579[a]
1,4-$(CH_3)_2$Az	595[a]
1,8-$(CH_3)_2$Az	599[a]
18	592

[a] Reference 4a.

establish that **18** is 1,8 disubstituted rather than 4,5 disubstituted.

Experimental Section[20]

1,4-Dimethylpyridinium Iodide.—To a solution of 93.0 g (1.00 mol) of 4-picoline in 500 ml of absolute ethanol was added 141.0 g (1.00 mol) of methyl iodide over a 15-min period. After stirring for 1 hr at room temperature and 1 hr heating under reflux, cooling the mixture gave 212 g (90%) of white needles of the product, which were filtered and washed with ether, mp 153.0–153.5° (lit.[21] mp 157–158°). The hygroscopic needles were stored in a desiccator until used.

6-Methylazulene.—This compound was prepared following the procedure similar to that given for the synthesis of 5,6-dimethylazulene.[22] To 100 ml of absolute ethanol[23] was added 5.1 g (0.22 g-atom) of sodium. After reaction and dissolution, the solution was cooled to ice-bath temperature and maintained under a nitrogen atmosphere while 14.5 g (0.22 mol) of freshly distilled cyclopentadiene was added. After 0.5 hr of stirring, 15.8 g (67.4 mmol) of 1,4-dimethylpyridinium iodide was added through Gooch tubing. The mixture was stirred for 1 hr at ice-bath temperature and 3.5 hr at room temperature. Heating to 60° resulted in formation of a hard, black mass which prevented adequate stirring. Distilled diethylene glycol (200 ml) was added and the product was removed by steam distillation with superheated steam (steam temperature, 300–325°; flask temperature, 130–140°, maintained by a heating mantle); steam distillation was continued until no further blue color appeared in the Eastman condensers with approximately 4 l. of distillate collected. The distillate was diluted with an equal volume of water and extracted with petroleum ether (bp 30–60°). The organic layer was washed with 200 ml of water, 200 ml of 10% hydrochloric acid, and two 200-ml portions of water. After drying ($MgSO_4$), concentration to about 25 ml volume, and standing overnight in a freezer, 1.30 (14%) of 6-methylazulene was obtained by filtration: mp 81.0–81.8° (lit.[24] mp 80°); nmr (CCl_4, internal TMS) τ 1.94 [d (J = 10.5 Hz), 2], 2.33 [t (J = 3.5 Hz), C_2 H, 1], 2.81 [d (J = 3.5 Hz), C_1 and C_3 H's, 2], 3.08 [d (J = 10.5 Hz), 2], and 7.60 (s, CH_3, 3).

A variety of modifications of the above method failed to improve the yield of 6-methylazulene; in fact, most attempts led to lower yields of product.

4-Methylazulene.—This hydrocarbon was prepared by the reported procedure of adding methyllithium to azulene (in tetrahydrofuran) followed by dehydrogenation of the dihydro product with chloranil[25] in 82% yield as a blue oil, nmr (CCl_4, internal TMS) τ 1.7–3.3 (m, ring H's, 7) and 7.10 (s, CH_3, 3).

4-Azulylacetic Acid (4).—To 1.06 g (7.5 mmol) of 4-methylazulene in 50 ml of dry ether under a dry nitrogen atmosphere was added 11.2 ml (7.5 mmol) of 0.66 M sodium N-methylanilide in ether[6a] at −15°. On standing, a golden precipitate was formed. Dry CO_2 was bubbled into the mixture and the color changed immediately to blue; CO_2 addition was continued for 20 min. Addition of water followed by extraction with ether gave 103 mg (10%) of recovered 4-methylazulene.

Acidification of the basic, aqueous layer followed by ether extraction gave 0.93 g (67%) of **4** after solvent evaporation, which was recrystallized from ether–petroleum ether to give blue crystals: mp 123–125° dec; ir (KBr) 5.9 μ (C=O); nmr (DMSO-d_6, internal TMS) τ −2 to 0 (broad s, OH, 1), 1.2–3.0 (m, Az H's, 7), and 5.74 (s, CH_2, 2); visible–uv (CH_2Cl_2) 677 nm (log ϵ 2.08), 617 (2.52), 575 (2.60), 356 (3.14), 343 (3.68), 329 (3.54), 286 (4.67), and 280 (4.68); mass spectrum (70 eV, direct) m/e (rel intensity) 186 (100) and 142 (19).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.15; H, 5.33.

Methyl 4-Azulylacetate.—Ethereal diazomethane was used to convert 50 mg (0.27 mmol) of 4-azulylacetic acid to its ester. Chromatography on basic alumina (CH_2Cl_2 eluent) gave 53 mg (98%) of the desired ester as a blue oil: ir (neat) 5.71 μ (C=O); nmr (CCl_4, internal TMS) τ 1.7–3.7 (m, Az H's, 7), 5.97 (s, CH_2, 2), and 6.43 (s, CH_3, 3); visible-uv (cyclohexane) 688 nm (OD 0.206), 650 (sh), 626 (0.529), 597 (0.592), 576 (0.598), 555 (sh), 356 (0.023), 344 (0.058), 302 (0.062), 286 (0.571), 280 (0.578), and 276 (sh); mass spectrum (70 eV, direct) m/e (rel intensity) 200 (100) and 141 (41).

This oil was converted to its 1,3,5-trinitrobenzene complex, which after recrystallization from ethyl acetate–petroleum ether gave brown needles, mp 134–135°.

Anal. Calcd for $C_{19}H_{15}N_3O_8$: C, 55.21; H, 3.66. Found: C, 55.27; H, 3.83.

4-Azulylethanol (6-OH).—To 145 mg (0.78 mmol) of acid **4** and 228 mg (6.0 mmol) of sodium borohydride in 25 ml of dry tetrahydrofuran was added dropwise 3 ml of boron trifluoride etherate dissolved in 20 ml of tetrahydrofuran and stirring was continued for an additional 45 min. This procedure and work-up was similar to that reported for the synthesis of 2-(1-azulyl)ethanol.[26] Chromatography of the product on basic alumina (CH_2Cl_2 eluent) gave 121 mg (92%) of **6-OH** initially as a blue oil which crystallized from carbon tetrachloride–petroluem ether: mp 58–59°; nmr (CCl_4, internal TMS) τ 1.6–3.3 (m, Az H's, 7), 6.18 [t (J = 7 Hz), α-CH_2, 2], 6.73 [t (J = 7 Hz), β-CH_2, 2], and 7.67 (s, OH, 1); visible–uv (CCl_4) 667 nm (log ϵ 2.14), 615 (2.55), 588 (2.59), 569 (2.61), 356 (3.50), 344 (3.79), 331 (3.69), and 281 (4.62); mass spectrum (70 eV, direct) m/e (rel intensity) 172 (100) and 143 (51).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.50; H, 6.90.

2-(4-Azulyl)ethyl Acetate (6-OAc).—A solution of 236 mg (1.37 mmol) of **6-OH** and 3 ml of acetic anhydride in 20 ml of dry pyridine was stirred at 0° for 12 hr. The cold solution was dissolved in 100 ml of methylene chloride, which was washed with two 20-ml portions of cold 10% hydrochloric acid and three 25-ml portions of cold water and dried ($MgSO_4$). Solvent evaporation and chromatography of the residue on basic, activity III–IV

(17) It is possible that hydrocarbon **16** was produced in the buffered acetolysis of **6**-ONs (possibly also from **6**-OTs) but decomposed during the product study.

(18) W. Triebs and H. Froitzheim, *Justus Liebigs Ann. Chem.*, **564**, 43 (1949).

(19) The methyl group resonances for 1-, 4-, 5-, and 6-methylazulene appear at τ 7.35, 7.10, 7.48, and 7.60, respectively, in carbon tetrachloride.

(20) All melting points were taken on a Kofler hot stage. Infrared, uv–visible, nmr, and mass spectra were recorded using P-E 137, Cary 11, Varian A-60 or T-60, and AEI MS-9 instruments, respectively. The alumina used was Alcoa F-20 basic alumina presumed to be activity I from the can. Microanalyses were determined by Galbraith Laboratories, Inc., or by M. M. Kim in this department using a Hewlett-Packard Model 185 C, H, N analyzer.

(21) E. D. Bergmann, F. E. Crane, and R. M. Fuoss, *J. Amer. Chem. Soc.*, **74**, 5979 (1952).

(22) C. W. Muth, M. L. DeMatte, A. R. Urbanik, and W. G. Isner, *J. Org. Chem.*, **31**, 3013 (1966).

(23) R. H. Manske, *J. Amer. Chem. Soc.*, **53**, 1106 (1931).

(24) P. A. Plattner and A. Studer, *Helv. Chim. Acta*, **29**, 1432 (1946).

(25) K. Hafner and H. Welds, *Justus Liebigs Ann. Chem.*, **606**, 90 (1957).

(26) A. G. Anderson, R. G. Anderson, and T. S. Fujita, *J. Org. Chem.*, **27**, 5435 (1962).

alumina[27] (CH_2Cl_2 eluent) yielded 282 mg (96%) of **6-OAc** as a blue oil: ir (neat) 5.74 μ (C=O); nmr (CCl_4, internal TMS) τ 1.7–3.3 (m, Az H's, 7), 5.64 [t (J = 7 Hz), α-CH_2, 2], 6.61 [t (J = 7 Hz), β-CH_2, 2], and 8.12 (s, CH_3, 3); visible-uv (cyclohexane) 684 nm (log ϵ 2.30), 622 (2.53), 594 (2.53), 573 (2.57), 555 (2.45), 350 (3.53), 342 (4.02), 330 (3.90), 284 (4.03), 279 (4.04), and 242 (3.76); mass spectrum (70 eV, direct) m/e (rel intensity) 214 (100), 171 (52), 154 (68), and 153 (74).

The oil was converted to its 1,3,5-trinitrobenzene complex, which was recrystallized from ethyl acetate–petroleum ether, mp 81–82°.

Anal. Calcd for $C_{20}H_{17}N_3O_8$: C, 56.21; H, 4.01; N, 9.83. Found: C, 56.26; H, 4.13; N, 9.63.

2-(4-Azulyl)ethyl Tosylate (6-OTs).—To a solution of 240 mg (1.40 mmol) of **6-OH** in 20 ml of dry ether at 0° was added 294 mg (1.54 mmol) of sublimed *p*-toluenesulfonyl chloride and 234 mg (4.2 mmol) of powdered potassium hydroxide in approximately three equal portions. After stirring for 3 hr at 0°, the ether layer was washed with three 20-ml portions of ice–water and dried ($MgSO_4$). Concentration and chromatography of the resultant blue oil on basic, activity III–IV alumina[27] (CH_2Cl_2 eluent) gave 340 mg (75%) of **6-OTs** initially as a blue oil which crystallized from ether–petroleum ether as blue crystals: mp 69.5–70.0°; ir (KBr) 7.4 and 9.3 μ; nmr ($CDCl_3$, internal TMS) τ 1.5–3.2 (m, ring H's, 11), 5.59 [t (J = 7 Hz), α-CH_2, 2], 6.53 [t (J = 7 Hz), β-CH_2, 2], and 7.74 (s, CH_3, 3); visible-uv (CH_2Cl_2) 674 nm (log ϵ 2.16), 615 (2.55), 572 (2.61), 355 (3.18), 342 (3.70), 286 (4.64), and 280 nm (4.68); mass spectrum (70 eV, direct) m/e (rel intensity) 326 (56) and 171 (100).

Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.90; H, 5.57. Found: C, 69.73; H, 5.56.

2-(4-Azulyl)ethyl Nosylate (6-ONs).—To a solution of 235 mg (1.36 mmol) of **6-OH** in 20 ml of dry ether at −20° was added 0.73 ml (1.22 mmol) of 1.67 M methyllithium in hexane (Foote). To the resultant cloudy solution was then added 314 mg (1.36 mmol) of sublimed *p*-nitrobenzenesulfonyl chloride. After 2 min the solution had clarified and was immediately poured onto a basic alumina column, where methylene chloride eluted 324 mg (67%) of **6-ONs**. Recrystallization from methylene chloride–petroleum ether gave brown needles: mp 108.5–109.5°; ir (KBr) 6.50, 7.30, 7.40, 8.43 μ; nmr ($CDCl_3$, internal TMS) τ 1.6–3.2 (m, ring H's, 11), 5.34 [t (J = 7 Hz), α-CH_2, 2] and 6.64 [t (J = 7 Hz), β-CH_2, 2]; visible-uv (CH_2Cl_2) 676 nm (log ϵ 2.08), 616 (2.46), 571 (2.56), 343 (3.62), 329 (3.48), 285 (4.63), and 280 (4.66).

Anal. Calcd for $C_{18}H_{15}NO_5S$: C, 60.49; H, 4.23. Found: C, 60.32; H, 4.35.

4-Vinylazulene–1,3,5-Trinitrobenzene Complex (12-TNB).—To 30 mg (0.092 mmol) of **6-OTs** in 10 ml of dry *tert*-butyl alcohol under a nitrogen atmosphere at 25° was added 2 ml (0.5 mmol) of 0.05 M potassium *tert*-butoxide in *tert*-butyl alcohol. After stirring for 15 min, 30 ml of ether was added, and the ether layer was separated, washed with three 10-ml portions of water, and dried ($MgSO_4$). Solvent concentration gave a blue oil which was chromatographed on basic alumina (petroleum ether eluent) to give 11 mg (77%) of 4-vinylazulene (**12**).

This compound was converted to its 1,3,5-trinitrobenzene complex and after recrystallization from ethyl acetate–petroleum ether was obtained as brown crystals: mp 142–143° (sublimation); ir (KBr) 6.13, 6.47, and 7.42 μ; nmr ($CDCl_3$, internal TMS) τ 0.70 (s, TNB H's, 3), 1.6–3.2 (m, Az H's and α-vinyl H, 8), and 3.7–4.5 (m, β-vinyl H's, 2); visible-uv (CH_2Cl_2) 713 nm (log ϵ 2.06), 644 (2.55), 5.92 (2.64), 347 (3.61), 292 (4.55), and 261 (4.53).

Anal. Calcd for $C_{18}H_{13}N_3O_6$: C, 58.86; H, 3.57. Found: C, 58.87; H, 3.51.

6-Azulylacetic Acid (5).—As in the preparation of acid **4**, 852 mg (6.0 mmol) of 6-methylazulene in 40 ml of ether was allowed to react with 10 ml of 0.680 M sodium N-methylanilide in ether at −20°. Warming to 5–10° caused the color of the solution to change to red. Carbonation at 0–10° and work-up gave 122 mg of 6-methylazulene and 958 mg (86%; 97% net yield) of **5**. A portion of **5** was chromatographed on deactivated (15% water) silica gel with ethyl acetate and the product was recrystallized from methylene chloride–hexane to give pure **5** as blue plates, mp 132–134° dec (lit.[6a] mp 126–127° dec).

Methyl 6-Azulylacetate.—**5** (50 mg, 0.28 mmol) was converted to the methyl ester with diazomethane in ether. Chromatography of the crude ester on basic alumina (CH_2Cl_2 eluent) gave 52 mg (97%) of the ester: mp 38–39°; ir (neat) 5.69 μ (C=O); nmr (CCl_4, internal TMS) τ 1.91 [d (J = 10 Hz), C_4 and C_8 H's, 2], 2.29 [t (J = 4 Hz), C_2 H, 1], 2.80 [d (J = 4 Hz), C_1 and C_3 H's, 2], 3.05 [d (J = 10 Hz), C_5 and C_7 H's, 2], 6.38 (s, CH_2, 2), and 6.42 (s, CH_3, 3); visible-uv (cyclohexane) 684 nm (log ϵ 1.98), 620 (2.42), 591 (2.45), 573 (2.49), 344 (3.80), 337 (3.62), 330 (3.65), 285 (4.86), and 279 mm (4.86); mass spectrum (70 eV, heated inlet) m/e (rel intensity) 201 (14), 200 (100), 141 (56), 139 (13), and 115 (27).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.14; H, 6.11.

2-(6-Azulyl)ethanol (7-OH). Method A.—Following the procedure used for **6-OH**, 147 mg (0.79 mmol) of **5** was reduced with diborane to give 123 mg (91%) of **7-OH**: mp 78–80°; nmr ($CDCl_3$, internal TMS) τ 1.80 [d (J = 10 Hz), C_4 and C_8 H's, 2], 2.16 [t (J = 4 Hz), C_2 H, 1], 2.55 [d (J = 4 Hz), C_1 and C_3 H's, 2], 2.86 [d (J = 10.5 Hz), C_5 and C_7 H's, 2], 6.13 [t (J = 6 Hz), α CH_2, 2], 7.05 [t (J = 6 Hz), β-CH_2, 2], and 8.20 (broad s, OH, 1); visible-uv (CH_2Cl_2) 672 nm (log ϵ 1.98), 610 (2.42), 565 (2.50), 344 (3.74), 336 (3.55), 329 (3.57), 286 (4.79), and 280 nm (4.80); mass spectrum (70 eV, heated inlet) m/e (rel intensity) 172 (100), 142 (22), 141 (68), and 115 (30).

Method B.—To a stirred solution of 1.00 g (7.05 mmol) of 6-methylazulene in 20 ml of dry ether under a nitrogen atmosphere at −20° was added 14.8 ml of 0.50 M sodium N-methylanilide in ether. A gold precipitate formed in the mixture, to which was added 212 mg (7.05 mmol) of paraformaldehyde through Gooch tubing. The mixture was allowed to warm to 25° and stirring was continued for 2 hr. The reaction mixture was diluted with water and ether, and the ether layer was separated, washed with four 100-ml portions of 5% hydrochloric acid, and dried ($MgSO_4$). Solvent concentration and chromatography of the blue residue on basic alumina gave two fractions; hexane eluted 900 mg of 6-methylazulene and chloroform eluted 110 mg (9%; 91% net yield) of **7-OH**, mp 78–79°, identical in all respects with the product from method A.

2-(6-Azulyl)ethyl Acetate (7-OAc).—Following the above method used for **6-OAc**, 147 mg (0.86 mmol) of **7-OH** yielded 135 mg (74%) of **7-OAc** as a blue oil: ir (neat) 5.86 μ (C=O); nmr (CCl_4, internal TMS): τ 1.95 [d (J = 10.5 Hz), C_4 and C_8 H's 2), 2.28 [t (J = 4 Hz), C_2 H, 1], 2.80 [d (J = 4 Hz), C_1 and C_3 H's, 2], 3.11 [d (J = 10.5 Hz), C_5 and C_7 H's, 2], 5.76 [t (J = 7.5 Hz), α-CH_2, 2], 7.05 [t (J = 7.5 Hz), β-CH_2, 2], and 8.08 (s, CH_3, 3); mass spectrum (70 eV, heated inlet) m/e (rel intensity) 214 (47), 154 (100), 153 (25), 141 (16), and 115 (16).

Acetate **7-OAc** was converted to its 1,3,5-trinitrobenzene complex in ethyl acetate which was recrystallized from ethyl acetate–hexane: mp 104.2–105.0°; visible-uv (CH_2Cl_2) 676 nm (log ϵ 1.99), 612 (2.42), 588 (2.47), 569 (2.50), 344 (3.74), 336 (3.56), 329 (3.59), 285 (4.79), and 279 (4.79).

Anal. Calcd for $C_{20}H_{17}N_3O_8$: C, 56.21; H, 4.01. Found: C, 56.36; H, 4.22.

2-(6-Azulyl)ethyl Tosylate (7-OTs).—Following the procedure used in the synthesis of **6-OTs**, 100 mg (0.58 mmol) of **7-OH** gave 168 mg (88%) of **7-OTs** as blue plates after recrystallization from methylene chloride–hexane: mp 107.5–108.5°; ir (KBr) 7.51 and 8.53 μ; nmr ($CDCl_3$, internal TMS) τ 1.86 [d (J = 10.5 Hz), C_4 and C_8 H's, 2], 2.12 [t (J = 4 Hz), C_2 H, 1], 2.45 [d (J = 8 Hz), tosyl H's, 2], 2.66 [d (J = 4 Hz), C_1 and C_3 H's, 2], 3.00 [d (J = 8 Hz), tosyl H's, 2], 3.12 [d (J = 10.5 Hz), C_5 and C_7 H's, 2], 5.67 [t (J = 6.5 Hz), α-CH_2, 2], 6.92 [t (J = 6.5 Hz), β-CH_2, 2], and 7.72 (s, CH_3, 3); visible-uv (CH_2Cl_2) 681 nm (log ϵ 2.00), 620 (2.42), 588 (2.47), 571 (2.49), 344 (3.73), 336 (3.56), 330 (3.58), 285 (4.77), and 279 (4.76); mass spectrum (70 eV, heated inlet) m/e (rel intensity) 326 (64), 154 (100), 141 (18), 115 (15), and 91 (15).

Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56. Found: C, 69.75; H, 5.37.

2-(6-Azulyl)ethyl Nosylate (7-ONs).—The procedure was that used in the preparation of **6-ONs** where 180 mg (1.05 mmol) of **7-OH** gave 220 mg (59%; 73% net yield) of **7-ONs** as black needles: mp 155° dec; ir (KBr) 7.41 and 8.49 μ; nmr (DMSO-d_6, internal TMS) τ 1.71–2.26 (m, 7), 2.70 [d (J = 4 Hz), 2], 2.98 [d (J = 11 Hz), 2], 5.46 [t (J = 6 Hz), α-CH_2, 2], and 6.86 [t (J = 6 Hz), β-CH_2, 2]; visible-uv (CH_2Cl_2) 684 nm (log ϵ 1.98), 622 (2.41), 5.90 (2.45), 573 (2.48), 344 (3.80), 337 (3.65), 330 (3.67), 285 (3.67), and 279 nm (4.85). An analytical sample was recrystallized from methylene chloride–hexane, mp 155° dec.

(27) Made by addition of 5% water to activity I alumina.[20]

Anal. Calcd for $C_{15}H_{15}NO_5S$: C, 60.49; H, 4.23. Found: C, 60.22; H, 4.30.

6-Vinylazulene (13).—This compound was isolated from several product study runs on 7-OTs and 7-ONs and was characterized as follows: mp 111–113°; ir (KBr) 6.38 (m), 6.69 (m), 11.79 (s), and 13.24 μ (s); nmr (CCl_4, internal TMS) τ 1.91 [d (J = 10.5 Hz), C_4 and C_8 H's, 2], 2.29 [t (J = 4 Hz), C_2 H, 1], 2.79 [d (J = 4 Hz), C_1 and C_3 H's, 2], 2.90 [d (J = 10.5 Hz), C_5 and C_7 H's, 2], and 3.15–4.80 (seven lines, vinyl H's, 3).

The 1,3,5-trinitrobenzene complex was prepared and recrystallized several times from ethanol: mp 118–119.5°; visible–uv (cyclohexane) 752 nm (log ϵ 1.96), 708 (2.10), 672 (2.40), 639 (2.45), 613 (2.51), 592 (2.46), 372 (3.88), 363 (3.64), 355 (3.75), 347 (3.67), and 291 (4.80).

Anal. Calcd for $C_{18}H_{13}N_3O_6$: C, 58.85; H, 3.57. Found: C, 58.66; H, 3.51.

2-(4-Azulyl)ethanol-α,α-d_2 (6-α,α-d_2-OH).—Analogous to the preparation of 6-OH, 147 mg (0.79 mmol) of acid 4 was reduced but using 147 mg (3.5 mmol) of sodium borodeuteride (Merck). This gave 132 mg (96%) of the labeled alcohol. Comparison of the integrated α- and β-methylene nmr signals showed 1.80 atoms of deuterium at C_α of the ethyl side chain.

2-(4-Azulyl)ethyl-α,α-d_2 Nosylate (6-α,α-d_2-ONs).—As in the synthesis of 6-ONs, 81 mg (0.47 mmol) of 6-α,α-d_2-OH was converted to 81 mg (48%, 68% net yield) of the labeled nosylate. Multiple integrations of the methylene nmr signals showed 1.80 atoms of deuterium at C_α of the ethyl side chain.

2-(6-Azulyl)ethanol-α,α-d_2 (7-α,α-d_2-OH).—This was prepared by the procedure given above for 6-α,α-d_2-OH with the labeled alcohol isolated in 94% yield. Multiple integrations of the α- and β-methylene nmr signals showed the presence of 1.85 atoms of deuterium at C_α of the ethyl side chain.

2-(6-Azulyl)ethyl-α,α-d_2 Tosylate (7-α,α-d_2-OTs).—Following the procedure given for the synthesis of 7-OTs, 177 mg (10 mmol) of the labeled alcohol produced 196 mg (59%, 93% net yield) of the labeled tosylate. Multiple integrations of the α- and β-methylene nmr signals showed the presence of 1.87 atoms of deuterium at C_α of the ethyl side chain.

2-(6-Azulyl)ethyl-α,α-d_2 Nosylate (7-α,α-d_2-ONs).—Following the above procedure for the synthesis of 7-ONs, 100 mg (0.58 mmol) of the labeled alcohol gave 105 mg (52%) of the labeled nosylate. Multiple integrations of the α- and β-methylene nmr signals showed the presence of 1.83 atoms of deuterium at C_α of the ethyl side chain.

3-(4-Azulyl)-1-propanol (8-OH).—To a solution of 294 mg (2.1 mmol) of 4-methylazulene in 20 ml of dry tetrahydrofuran at 0° under a nitrogen atmosphere was added 2.96 ml (2.1 mmol) of 0.71 M sodium N-methylanilide in ether followed by 2 ml (42 mmol) of ethylene oxide. The solution showed no immediate color change but after stirring for 4 hr had become blue-green. An additional 1 ml of ethylene oxide was added and stirring was continued for 1 hr. Water (20 ml) was added to the blue reaction mixture, which was then extracted with 50 ml of ether. The ether layer was washed with two 50-ml portions of cold 10% hydrochloric acid and three 50-ml portions of water, and dried ($MgSO_4$). Solvent evaporation and chromatography on basic activity II–III alumina[28] (1:1 CH_2Cl_2–$CHCl_3$ eluent) gave 130 mg (33%, 59% net yield) of 8-OH as a blue oil.

This was converted to its 1,3,5-trinitrobenzene complex, which after recrystallization from ethyl acetate–petroleum ether was brown needles: mp 108–109°; ir (KBr) 3.03 (OH), 6.45, 7.40, and 9.29 μ; nmr ($CDCl_3$, internal TMS) τ 0.86 (s, TNB H's, 3), 1.6–3.2 (m, Az H's, 7), 6.26 [t (J = 6 Hz), α CH_2, 2], 6.68 [t (J = 7 Hz), δ CH_2, 2], 7.88 (m, β CH_2, 2), and 8.42 (s, OH, 1); visible–uv (CH_2Cl_2) 657 nm (sh), 670 (sh), 566 (log ϵ 2.64), 355 (sh), 343 (3.75), 329 (3.63), 285 (4.73), and 280 (4.73); mass spectrum (70 eV, direct) m/e (rel intensity) 186 (19) and 142 (100).

Anal. Calcd. for $C_{19}H_{17}N_3O_7$: C, 57.15; H, 4.29; N, 10.52. Found: C, 57.50; H, 4.46; N, 10.28.

3-(4-Azulyl)-1-propyl Acetate (8-OAc).—A solution containing 200 mg (1.1 mmol) of 8-OH and 1 ml of acetic anhydride in 10 ml of dry pyridine was allowed to stand for 24 hr and worked up as given in the preparation of 6-OAc. Chromatography on basic, activity II–III alumina[28] (CH_2Cl_2 eluent) gave 225 mg (93%) of 8-OAc as a blue oil. The 1,3,5-trinitrobenzene complex was prepared and recrystallized from ethyl acetate–petroleum ether to give brown needles: mp 92–93°; ir (KBr) 5.71 μ (C=O); nmr ($CDCl_3$), internal TMS) τ 0.88 (s, TNB H's, 3), 1.7–3.2 (m, Az H's, 7), 5.84 [t (J = 6 Hz), α CH_2, 2], 6.72 [t (J = 7 Hz), δ CH_2, 2], and 7.5–8.1 (m, β CH_2 and CH_3 at τ 7.96, 5); visible–uv (CH_2Cl_2) 656 nm (sh), 605 (sh), 563 (log ϵ 2.56), 352 (3.46), 342 (3.92), 330 (3.82), 286 (4.89), and 280 (4.89).

Anal. Calcd for $C_{21}H_{19}N_3O_8$: C, 57.14; H, 4.34; N, 9.52. Found: C, 57.51; H, 4.53; N, 9.34.

3-(4-Azulyl)-1-propyl Nosylate (8-ONs).—Using the procedure described for the synthesis of 6-ONs, 117 mg (0.63 mmol) of 8-OH produced 156 mg (63%) of 8-ONs as a blue oil: ir (neat) 3.28, 6.49, and 8.48 μ; nmr ($CDCl_3$, internal TMS) τ 1.5–3.2 (m, ring H's, 11), 5.81 [t (J = 6 Hz), α CH_2, 2], 6.68 [t (J = 7 Hz), γ CH_2, 2], and 7.73 (m, β CH_2, 2).

The 1,3,5-trinitrobenzene complex was prepared and recrystallized from ethyl acetate–petroleum ether as brown needles: mp 101–103°; visible–uv (CH_2Cl_2) 605 nm (sh), 568 (log ϵ 2.63), 343 (3.72), 285 (4.67), and 280 (4.67).

Anal. Calcd for $C_{25}H_{20}N_4O_{11}S$: C, 51.37; H, 3.45; N, 9.59. Found: C, 51.70; H, 3.67; N, 9.32.

2-Phenylethyl Tosylate (9-OTs).—This compound was prepared by the usual method.[29] Recrystallization from methylene chloride–hexane gave white crystals, mp 38.5–39.0° (lit.[30] mp 37.5–38.2°).

2-Phenylethyl Nosylate (9-ONs).—Using the reaction conditions and work-up described for the synthesis of 6-ONs, 1.22 g (10 mmol) of 2-phenylethanol gave a white, crystalline residue after solvent evaporation which when recrystallized from methylene chloride–hexane gave 2.21 g (72%) of 9-ONs as white needles: mp 101.5–102°; nmr ($CDCl_3$, internal TMS) τ 1.71 [d (J = 9 Hz), nosyl H's, 2], 2.12 [d (J = 9 Hz), nosyl H's, 2], 2.80 (m, phenyl H's, 5), 5.67 [t (J = 6.5 Hz), α CH_2, 2], and 7.01 [t (J = 6.5 Hz), β CH_2, 2].

Anal. Calcd for $C_{14}H_{13}NO_5S$: C, 54.71; H, 4.26. Found: C, 54.75; H, 4.18.

2-(p-Anisyl)ethyl Tosylate (10-OTs).—Large white needles of this compound were prepared by the usual method,[29] mp 57–58° (lit.[31] mp 57–58°).

2-(p-Anisyl)ethyl Nosylate (10-ONs).—Following the above procedure for synthesis of 9-ONs, 1.52 g (10 mmol) of 2-(p-anisyl)ethanol produced 2.48 g (74%) of 10-ONs as bright yellow needles: mp 97–97.5°; nmr ($CDCl_3$, internal TMS) τ 1.71 [d (J = 9.5 Hz), nosyl H's, 2], 2.08 [d (J = 9.5 Hz), nosyl H's, 2], 2.96 [d (J = 9 Hz), anisyl H's, 2], 3.24 [d (J = 9 Hz), anisyl H's, 2], 5.68 [t (J = 6.5 Hz), α CH_2, 2], 6.25 (s, OCH_3, 3), and 7.08 [t (J = 6.5 Hz), β CH_2, 2].

Anal. Calcd for $C_{15}H_{15}NO_6S$: C, 53.40; H, 4.48. Found: C, 53.45; H, 4.60.

Ethyl Tosylate (11-OTs).—Absolute ethanol was converted by the ether–powdered potassium hydroxide technique, as with 6-OTs, to 11-OTs and was trap-to-trap distilled (130°, 0.1 mm) as a colorless oil which crystallized on standing. Recrystallization from ether–petroleum ether gave 59% of crystalline 11-OTs: mp 33.0–33.5° (lit.[32] mp 32.2–32.3°); nmr (CCl_4, internal TMS) τ 2.52 (A_2B_2 m, tosyl H's, 4), 5.94 (q, α CH_2, 2), 7.61 (s, CH_3, 3), and 8.77 (t, CH_3, 3).

Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04. Found: C, 53.96; H, 5.97.

Ethyl Nosylate (11-ONs).—As in the preparation of 6-ONs, absolute ethanol was converted to 11-ONs and was chromatographed on basic alumina (CH_2Cl_2 eluent) to give a 60% yield of 11-ONs. Recrystallization from methylene chloride–petroleum ether produced white crystals: mp 91.5–92.0°; ir (KBr) 6.52, 7.35, 7.44, and 8.44 μ; nmr (DMSO-d_6, internal TMS) τ 1.95 (A_2B_2 m, nosyl H's, 4), 5.60 (q, CH_2, 2), and 8.67 (t, CH_3, 3).

Anal. Calcd for $C_8H_9NO_5$: C, 41.56; H, 3.92; N, 6.06. Found: C, 41.21; H, 4.00; N, 5.91.

Kinetic Methods.—Dissolved gases in purified acetic acid (distilled from acetic anhydride) containing 1% by volume of acetic anhydride were replaced by nitrogen by the freeze–thaw technique (4–6 cycles). All dilutions and manipulations of solvent were carried out in a glove box in a dry, nitrogen atmosphere.

(28) Made by addition of 3% water to activity I alumina.[20]

(29) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(30) W. H. Saunders, S. Asperger, and D. H. Edison, *J. Amer. Chem. Soc.*, **80**, 2421 (1958).

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(32) H. R. McCleary and L. P. Hammett, *ibid.*, **63**, 2254 (1941).

Loaded 2-ml ampoules containing *ca.* 1.3 ml of solution were plugged, removed from the glove box, and sealed with a torch. About 1.1-ml samples were removed from the ampoules with a constant delivery pipette and diluted with a 9:1 mixture of acetic acid–acetic anhydride; for 0.01 *M* sulfonate ester, 10 ml of diluent was used while with 0.005 *M* substrate, 2 ml of diluent was added. Larger dilution volumes gave errant end-point readings during titrations. The titrant was perchloric acid in acetic acid containing 2% acetic anhydride.

All potentiometric titrations were carried out with a Metrohm Herisau E436D Potentiograph automatic titrator using an EA 147X micro, combination electrode. By comparison to the titrations for a standard buffer solution, the end points were taken at the same millivolt reading for all titrations for a particular solvolysis run (12–15 points over 2 half-lives). Two or more samples were titrated after 10 solvolytic half-lives and were taken as the extent of reaction at time infinity.

The buffer solutions were prepared by dissolving anhydrous potassium acetate in the acetic acid solvent. For the conductometric studies with 8-ONs, the solvent contained only 0.02% (v/v) of acetic anhydride. The conductivity method has been described[15] using the M-D Minicell;[33] the 3-ml working volume of this conductivity cell without significant loss of precision made these measurements with 8-ONs practical. The 120° temperature used with this method appears to be close to the maximum operating temperature for this solvent system in the conductivity method. Approximately 100 readings were taken on the bridge over about 2 half-lives for each run. It was interesting that the specific conductance of the runs with 8-ONs increased with time, whereas with tosylate esters in this solvent the specific conductance decreases (KOAc being replaced by KONs or KOTs).[15]

Rate constants were calculated using either a least-squares computer program (RATSOL2) developed by Professor K. Conrow or the LSKIN1 program[34] as modified for the IBM 360/50 system by Professor Conrow. Both programs gave essentially identical results.

Activation parameters and extrapolated rate data were calculated using a program developed by Professor Conrow. This program was written to calculate thermochemical data from rate data at two temperatures, giving a "best" value along with "maximum" and "minimum" values based on the errors associated with the rate data.

Preparative Buffered Acetolyses.—The general procedure employed for the preparative buffered acetolyses involved dissolving the arenesulfonate ester in potassium acetate buffered acetic acid of the same concentration as was employed in that ester's kinetic study. This solution was then loaded into a number of 10-ml ampoules in the glove box, which were plugged, removed, sealed, and placed in the constant-temperature bath for the appropriate time interval. The ampoules were then removed from the bath, quenched in ice–water, and opened, and the contents were combined and diluted with methylene chloride. After washing with several portions of water, saturated sodium bicarbonate solution, and water, the organic layer was dried ($MgSO_4$) and the solvent was evaporated. The residue could then be chromatographed and/or analyzed directly by nmr spectroscopy where multiple integrations of nmr absorptions were compared to those of an added standard compound, either 1,3,5-trinitrobenzene or dioxane. The results from such preparative runs are summarized in Table VI.

TABLE VI
SUMMARY OF PREPARATIVE BUFFERED ACETOLYSIS AT 120°

Starting material	Time ($t_{1/2}$)	Products (%)
6-OTs	1	6-OTs (50) + 12 (37) + 6-OAc (9)
6-ONs	1	6-ONs (50) + 12 (17) + 6-OAc (27)
7-OTs	1	7-OTs (37) + 13 (28) + 7-OAc (11)
7-ONs	1	7-ONs (47) + 13 (14) + 7-OAc (37)
8-ONs	10	18 (51) + 8-OAc (25)

TABLE VII
SUMMARY OF STABILITY TESTS FOR SOLVOLYTIC PRODUCTS AT 120°

Solvolytic product	Time ($t_{1/2}$)	Recovery (%)
6-OAc	1 (6-OTs)	6-OAc (72) + 12 (17)
	1 (6-ONs)	6-OAc (84) + 12 (6)
7-OAc	1 (7-OTs)	7-OAc (69) + 13 (25)
	1 (7-ONs)	7-OAc (82) + 13 (8)
13	1 (7-OTs)	13 (77)
	1 (7-ONs)	13 (84)
18	10 (8-ONs)	18 (67)
8-OAc	10 (8-ONs)	8-OAc (91)

Stability Tests for Solvolytic Products.—These product stability tests were carried out in the same manner as that described above for the preparative buffered acetolyses. The composition and amounts of the material(s) obtained from such tests were either from weights of isolated compounds or from multiple integrations of nmr spectral absorptions using an added standard. These results are summarized in Table VII.

Registry No.—**4,** 26157-13-1; **4** methyl ester, 26157-17-5; **4** methyl ester TNB, 38304-97-1; **5,** 26157-15-3; **5** methyl ester, 26156-73-0; **6**-OH, 13935-44-9; **6**-OAc, 26154-66-5; **6**-OAc TNB, 38305-02-1; **6**-OTs, 26154-63-2; **6**-ONs, 38305-04-3; **7**-OH, 26157-10-8; **7**-OAc, 26154-68-7; **7**-OAc TNB, 38305-07-6; **7**-OTs, 26211-00-7; **7**-ONs, 38305-09-8; **8**-OH, 38305-10-1; **8**-OH TNB, 38305-11-2; **8**-OAc, 38305-12-3; **8**-OAc TNB, 38305-13-4; **8**-ONs, 36740-21-3; **8**-ONs TNB, 38305-15-6; **9**-ONs, 24760-80-3; **10**-ONs, 24760-81-4; **11**-OTs, 80-40-0; **11**-ONs, 15481-55-7; **12,** 38305-18-9; **12** TNB, 38305-19-0; **13,** 38305-20-3; **13** TNB, 38305-21-4; 4-methylazulene, 17647-77-7.

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(33) Available from R-M Research Products, Inc., 1820 Alabama, Manhattan, Kans. 66502.

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